Electronic Supplementary Information

Microwave-assisted one-pot synthesis of new ionic iridium complexes of $[Ir(bzq)_2(N\hat{}N)]^+A^-$ type and their selected electroluminescent properties

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Table 1S. Selected optimized ground-state parameters of 2FA' in gas phase and CH_3CN media at B3LYP/SDD level.

	gas	CH_3CN
	Bond lengths (Å)	
Ir-N15	2.104	2.104
Ir-N29	2.070	2.073
Ir-C49	2.125	2.123
	Bond angles (deg)	
N15-Ir-N49	88.4	88.6
C5-Ir-N19	96.0	95.4
C5-Ir-N29	89.9	90.2
N15-Ir-C5	79.6	79.6
N15-Ir-N19	174.0	173.5
N29-Ir-N49	173.9	173.5
C5-Ir-C59	172.3	172.5
N15-Ir-N29	96.1	96.0

Table 2S. Selected optimized ground-state parameters of 2FA' in CH_3CN media using B3LYP functional containing different basis sets

	Basis sets	Bond lengths (Å)
Ir-N15	6-31G*	2.104
	6-31++G**	2.104
	6-311++G**	2.104
Ir-N29	6-31G*	2.073
	6-31++G**	2.073
	6-311++G**	2.073
Ir-C49	6-31G*	2.105
	6-31++G**	2.105
	6-311++G**	2.105
	Basis sets	Valence angle (deg)
N15-Ir-N49	6-31G*	88.6
	6-31++G**	88.6
	6-311++G**	88.6
C5-Ir-N19	6-31G*	95.4
	6-31++G**	95.4
	6-311++G**	95.4
C5-Ir-N29	6-31G*	90.2
	6-31++G**	90.2
	6-311++G**	90.2
N15-Ir-C5	6-31G*	79.6
	6-31++G**	79.6
	6-311++G**	79.6
N15-Ir-N19	6-31G*	173.5
	6-31++G**	173.5
	6-311++G**	173.5
N15-Ir-N29	6-31G*	96.0
	6-31++G**	96.0
	6-311++G**	96.0
N29-Ir-N49	6-31G*	173.5
	6-31++G**	173.5
	6-311++G**	173.5
C5-Ir-C59	6-31G*	172.7
	6-31++G**	172.7
	6-311++G**	172.7

Table 3S. The energy levels and Homo-Lumo energy gaps for the studied complexes (in eV) calculated at the B3LYP/LANL2DZ/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	$E_g^{theor.}$ [eV]	$E_g^{exp.}$ [eV]
2AA’	-5,75	-2,48	3,27	2.40
2BA’	-5,72	-2,42	3,29	2.21
2CA’	-5,79	-2,44	3,35	2.20
2DA’	-5,69	-2,38	3,31	2.24
2EA’	-5,59	-2,32	3,27	1.73
2FA’	-5,84	-2,44	3,40	2.40
2GA’	-5,82	-2,47	3,34	2.17
2HA’	-5,77	-2,43	3,34	2.09

Table 4S. The energy levels and Homo-Lumo energy gaps for the studied complexes (in eV) calculated at the M06/LANL2DZ/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	$\Delta E_{theor.}$ [eV]	$\Delta E_{exp.}$ [eV]
2AA’	-8,06	-5,22	2,84	2.40
2BA’	-8,15	-4,76	3,39	2.21
2CA’	-8,21	-4,82	3,39	2.20
2DA’	-8,10	-4,78	3,32	2.24
2EA’	-8,07	-4,59	3,47	1.73
2FA’	-8,03	-5,14	2,89	2.40
2GA’	-7,92	-4,66	3,25	2.17
2HA’	-8,00	-4,50	3,51	2.09

Table 5S. The HOMO-LUMO energy gaps for the studied complexes (in eV) calculated by ONIOM method using WB97XD functional containing different basis sets.

compound	E_1 [eV]	E_2 [eV]	E_3 [eV]	$E_g^{teor.}$ [eV]	$E_g^{exp.}$ [eV]
2AA’	9.62	6.21	9.13	2.17	2.40
2BA’	9.68	6.23	9.14	2.22	2.21
2CA’	9.53	6.30	9.05	2.32	2.20
2DA’	9.73	6.24	9.18	2.27	2.24
2EA’	9.80	6.04	9.10	1.83	1.73
2FA’	9.55	6.32	8.84	2.28	2.40
2GA’	9.46	6.10	8.85	2.32	2.17
2HA’	9.51	6.22	8.82	2.04	2.09

Table 6S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for **2FA'**.

Atom symbol	X	Y	Z
Ir	-0.04074265	-0.00041241	0.00005571
C	0.67372352	-4.39211403	-2.21606153
C	1.39406753	-3.96446035	-1.07822972
C	1.08915394	-2.68275189	-0.54445639
C	0.10531347	-1.81291059	-1.09526249
C	-0.57199609	-2.29084914	-2.21677343
C	-0.29082481	-3.56320364	-2.76805893
C	2.41340163	-4.75661981	-0.44267781
C	3.09156471	-4.30475701	0.65289019
C	2.80966455	-3.01304571	1.21738014
C	1.80570489	-2.22201657	0.60418346
C	3.46905801	-2.48383757	2.34463729
C	3.12060945	-1.22770838	2.81217491
C	2.11658236	-0.50128657	2.15803636
N	1.47212836	-0.97997218	1.08638983
C	-4.00901040	1.60821962	-2.31862031
C	-4.07749341	0.79638652	-1.16585796
C	-2.85581538	0.39261501	-0.58242881
N	-1.63649291	0.75514275	-1.08671679
C	-1.60113535	1.52448307	-2.17858177
C	-2.77014882	1.96681475	-2.81784162
C	-5.30391187	0.35961656	-0.55777116
C	-5.29897962	-0.42746080	0.55703077
C	-4.06721527	-0.84876013	1.16522816
C	-2.85066487	-0.42934244	0.58213160
C	-3.98863831	-1.65997311	2.31778287
C	-2.74539290	-2.00264540	2.81732881
C	-1.58195908	-1.54517343	2.17851968
N	-1.62689853	-0.77626206	1.08668482
H	-6.23219545	-0.75073552	1.00686437
H	-6.24111695	0.67113090	-1.00764493
H	-4.92220653	1.94198902	-2.80040629
H	-2.67877270	2.58857005	-3.70073132
H	-0.62095339	1.79158820	-2.55255440
H	-4.89762699	-2.00566890	2.79914611
H	-2.64627858	-2.62339995	3.70008768
H	-0.59855439	-1.79985557	2.55276980
H	1.81527359	0.48132454	2.49836289
H	3.60768892	-0.79120722	3.67638789
H	4.24395491	-3.06395623	2.83712261

H	3.85867450	-4.91480942	1.12051728
H	2.64047689	-5.73607918	-0.85545874
H	0.88266770	-5.36655317	-2.64888470
H	-0.84287304	-3.89643725	-3.64371120
H	-1.33778307	-1.68246109	-2.69471217
C	3.43693632	2.52870959	-2.34399353
C	2.77037254	3.04931242	-1.21696890
C	1.77671841	2.24521752	-0.60395664
N	1.45954937	0.99883809	-1.08611492
C	2.11072466	0.52847086	-2.15743996
C	3.10527026	1.26800247	-2.81136566
C	3.03511372	4.34469264	-0.65258011
C	2.35074257	4.78778331	0.44269967
C	1.34179464	3.98234894	1.07813224
C	1.05397779	2.69662888	0.54450014
C	0.61558762	4.40066362	2.21571410
C	-0.33793904	3.55912281	2.76774228
C	-0.60207463	2.28303917	2.21665916
C	0.08165168	1.81394165	1.09531037
H	2.56483203	5.77019153	0.85541323
H	3.79432013	4.96468217	-1.12004107
H	4.20425371	3.11890134	-2.83637661
H	3.59841470	0.83781141	-3.67529962
H	1.82282874	-0.45817962	-2.49773007
H	0.81145016	5.37791360	2.64832258
H	-0.89459866	3.88520224	3.64316794
H	-1.35990245	1.66465013	2.69446558

Table 7S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for **2GA'**.

Atom symbol	X	Y	Z
C	-4.37617909	3.71944412	-2.06713798
C	-4.05358308	3.05917198	-0.83163171
C	-3.03145770	2.07687492	-0.84724833
C	-2.33615523	1.74117657	-2.05139728
C	-2.67990010	2.41409777	-3.25556031
C	-3.71755091	3.41045348	-3.22257271
C	-1.97786787	2.06225858	-4.43012443
C	-0.99262204	1.08846859	-4.37393084
C	-0.67317267	0.43268591	-3.16171160
C	-4.69013047	3.32893442	0.39620848
C	-4.30264553	2.63827599	1.53223399
C	-3.28251566	1.68164496	1.44455978
H	-5.15794854	4.47310987	-2.05958374
H	-3.97493564	3.92116240	-4.14683913
H	0.10821986	-0.32508513	-3.17959028
H	-2.21632791	2.55749423	-5.36733154
H	-0.45405827	0.82156975	-5.28020499
H	-5.47805399	4.07503284	0.44250431
H	-4.77142630	2.82135736	2.49212257
H	-2.95166502	1.12595341	2.31289089
C	-4.28273688	-2.77769181	-1.34518055
C	-4.58169451	-3.48118917	-0.19035300
C	-3.29574967	-1.78359940	-1.31229045
C	-3.88991456	-3.18658528	1.00137596
C	-4.12038824	-3.85661776	2.25216030
C	-2.90504404	-2.16759563	0.96196966
C	-3.41111477	-3.52256278	3.37005012
C	-2.15722683	-1.80574074	2.12640223
C	-2.40980046	-2.48938954	3.34691832
C	-1.65745926	-2.11115953	4.48148833
C	-0.48497154	-0.43583190	3.14511336
C	-0.71328885	-1.10179860	4.37235929
H	-4.79600701	-2.97922819	-2.27824891
H	-5.34232199	-4.25645275	-0.19463921
H	-4.87362315	-4.63806984	2.28679702
H	-3.03318487	-1.21656017	-2.19654749
H	-3.59892199	-4.04107751	4.30661278
H	-1.82564159	-2.61399289	5.42984759
H	0.26707362	0.35098572	3.12110101
H	-0.13624729	-0.81424956	5.24812829
Ir	-1.12792435	-0.01248321	0.00694070
H	1.41614752	4.36406862	1.22299433

H	-0.59781832	2.98863113	0.82502594
C	0.38973913	2.56547041	0.69333912
C	1.53721382	3.33470768	0.90607839
C	2.81068975	2.79271392	0.75299489
N	0.45015056	1.27888660	0.33985270
C	2.89248453	1.42995808	0.33308860
C	1.68423427	0.71638730	0.15303002
N	0.47371427	-1.24753338	-0.41551754
C	1.69697416	-0.65329199	-0.25727238
C	4.11513887	0.74401350	0.02385836
C	0.43748363	-2.52021511	-0.81908104
C	2.91808050	-1.32629359	-0.49656957
H	-0.54174014	-2.96595809	-0.93773062
C	4.12711314	-0.56265526	-0.37051255
C	1.59917195	-3.25765893	-1.06499368
C	2.86219526	-2.69615208	-0.89696762
H	1.49774916	-4.29439500	-1.36423153
C	4.00525184	3.63149146	1.02075421
C	4.10186563	4.91233156	0.44978819
C	5.20151436	5.72653229	0.71881023
C	6.21433540	5.27953263	1.57095363
C	6.12224649	4.01310030	2.15329778
C	5.02838078	3.19212520	1.87937289
H	3.32221402	5.25972378	-0.22148557
H	5.26746382	6.70886244	0.26101959
H	7.06882039	5.91531040	1.78209291
H	6.89930232	3.66435211	2.82664397
H	4.95357628	2.21902717	2.35464170
C	4.07286962	-3.52002554	-1.13898159
C	5.09820128	-3.61267831	-0.18131083
C	6.20788642	-4.42608007	-0.41083831
C	6.31388623	-5.15251542	-1.59932734
C	5.29899698	-5.06957721	-2.55577799
C	4.18357064	-4.26498142	-2.32581984
H	5.01343939	-3.06979393	0.75488296
H	6.98671611	-4.49561783	0.34245101
H	7.18079345	-5.78145539	-1.77774455
H	3.40244109	-4.19563279	-3.07692001
H	5.37549362	-5.62973890	-3.48273653
H	5.04769125	1.29072985	0.08596495
H	5.06873732	-1.03666097	-0.61750085
C	-1.19599633	-0.76344921	1.99077298
N	-2.62050624	-1.48465394	-0.19522153
N	-2.65864932	1.40633476	0.29206400
C	-1.33181626	0.73457911	-1.96989786

Table 8S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for 2HA'.

Atom symbol	X	Y	Z
C	4.83341604	2.55261455	-2.98207193
C	3.60503050	1.82072905	-3.14334864
C	2.93255255	1.34474917	-1.98450027
C	3.48538315	1.63050700	-0.69614407
C	4.69325679	2.35877856	-0.55385179
C	5.35804776	2.80653678	-1.74732302
N	2.77513009	1.19288020	0.39386006
C	5.16258940	2.60892313	0.75096788
C	4.43757979	2.14664467	1.83661689
C	3.24661285	1.43990597	1.62149188
C	3.02362346	1.54624680	-4.40115994
C	1.83394929	0.83650504	-4.46490889
C	1.19249623	0.36558147	-3.29546407
C	1.72056300	0.59456553	-2.02402810
H	5.34595632	2.90683395	-3.87258653
H	6.28614708	3.36053468	-1.64292105
H	2.65256639	1.07053408	2.44775655
H	6.08525160	3.16334042	0.89536685
H	4.76871079	2.32240856	2.85355136
H	3.51142170	1.89566192	-5.30689918
H	1.38647478	0.63225116	-5.43480275
H	0.26505339	-0.19279844	-3.40909738
C	4.44506254	-2.82835655	-0.45682533
C	4.40474825	-3.50564168	0.75027681
C	3.49692771	-1.83170773	-0.71928224
C	3.42987290	-3.15907820	1.70623240
C	3.32208387	-3.77550761	3.00013685
C	2.51210627	-2.12823935	1.37730966
C	2.38129715	-3.36267520	3.89891477
C	1.53234810	-1.67644573	2.31552864
C	1.46851384	-2.29299023	3.59538300
C	0.69925707	-0.59256860	1.91798362
C	0.51394261	-1.80538812	4.51523987
C	-0.21247268	-0.14731586	2.87602302
C	-0.30574276	-0.74797749	4.15335248
N	2.53927425	-1.50310096	0.15585853
H	5.18965112	-3.05783111	-1.21015713
H	5.12143608	-4.29117987	0.97102016
H	4.01439187	-4.57418952	3.24917256
H	3.49256305	-1.29867342	-1.66114451

H	2.31837165	-3.83616023	4.87517039
H	0.43697844	-2.25666014	5.50056281
H	-0.87794455	0.68499935	2.65717883
H	-1.03332636	-0.36798745	4.86663913
Ir	1.08957826	0.01983970	-0.08312040
H	-1.49592286	4.58352787	0.58551921
C	-0.42608828	2.77363356	0.19418142
C	-1.59768817	3.51417843	0.44322175
C	-2.85472078	2.93937244	0.47815031
N	-0.47932877	1.44184962	-0.00696686
C	-2.92705083	1.53938440	0.22575913
C	-1.71940561	0.84334806	-0.03618865
N	-0.56259700	-1.15118584	-0.67600283
C	-1.76415420	-0.54520070	-0.39360934
C	-4.15225470	0.80055275	0.25903985
C	-0.58364594	-2.39773384	-1.18436849
C	-3.01112366	-1.21150649	-0.49241347
C	-4.19313803	-0.51592941	-0.08451069
C	-1.79731615	-3.09878613	-1.32164859
C	-3.01876253	-2.55432102	-0.96997688
H	-1.75729990	-4.09693239	-1.74192972
C	-4.04380441	3.78938134	0.74351712
C	-4.05413054	4.63854255	1.86328376
C	-5.14288677	5.47500091	2.10853273
C	-6.23068274	5.48609945	1.23227500
C	-6.22484904	4.65525795	0.10924715
C	-5.14198462	3.81012126	-0.13393496
H	-3.21354857	4.62817084	2.55076020
H	-5.14082972	6.11693942	2.98424954
H	-7.07658623	6.13998218	1.42167383
H	-7.06126554	4.66777865	-0.58298837
H	-5.13664702	3.18419157	-1.02079439
C	-4.25662366	-3.35993249	-1.13263767
C	-5.34613619	-2.88777666	-1.88522610
C	-6.47781455	-3.68318760	-2.06569485
C	-6.54147187	-4.95627278	-1.49405494
C	-5.46281829	-5.43563747	-0.74707526
C	-4.32572738	-4.64691333	-0.57253794
H	-5.29714015	-1.90853767	-2.35109143
H	-7.30736026	-3.30909943	-2.65803454
H	-7.42514956	-5.57189231	-1.63238075
H	-3.49193676	-5.02022191	0.01462193
H	-5.50550872	-6.42363638	-0.29873200
H	-5.05804264	1.30860221	0.56456157
H	-5.13135975	-1.05509315	-0.05398862
C	0.87026600	3.52459352	0.13025586

H	1.45023693	3.22657291	-0.74274729
H	1.47651726	3.35259359	1.02272469
H	0.66891049	4.59485155	0.06539819
C	0.67252988	-3.06682239	-1.65784250
H	1.32205908	-2.35521224	-2.16715246
H	0.41603774	-3.86965414	-2.35158386
H	1.22688066	-3.51182306	-0.82762666

Table 9S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for **2AA'**.

Atom symbol	X	Y	Z
Ir	0.03254530	0.19326957	0.01063120
C	-4.40781011	-0.27612737	-2.23171768
C	-4.02543670	-1.04112653	-1.11065692
C	-2.73261223	-0.81956257	-0.57172360
N	-1.87404266	0.09797345	-1.10987770
C	-2.26297548	0.80929066	-2.17064157
C	-3.52549351	0.65029342	-2.76173665
C	-4.86304974	-2.02729205	-0.48630998
C	-4.42370088	-2.73349212	0.59593874
C	-3.11484716	-2.52368331	1.15687220
C	-2.25971739	-1.55354998	0.56500551
C	-2.63746290	-3.24061017	2.27640283
C	-1.36601551	-2.98324395	2.76232330
C	-0.53056653	-2.01344862	2.16330702
C	-0.94879567	-1.27129496	1.05815928
C	1.74062658	4.22936232	-2.29096564
C	0.93471352	4.29084265	-1.15759815
C	0.48828695	3.10482767	-0.56623304
N	0.82897336	1.89713429	-1.08531570
C	1.60913933	1.84108888	-2.17737585
C	2.08614319	2.98331863	-2.81189538
C	-0.81674984	4.20446533	1.30121678
C	-0.36690702	3.05946672	0.63818187
C	-1.61675350	4.08233871	2.43261164
C	-1.95447424	2.80799733	2.88309884
C	-1.48069722	1.70300689	2.18679433
N	-0.70505347	1.81622530	1.08996169
H	2.09328410	5.14276162	-2.75748685
H	2.71281795	2.88894568	-3.69103342
H	1.84914825	0.84923388	-2.54246580
H	-1.96780542	4.96783942	2.95095123
H	-2.57386223	2.65962804	3.75987471
H	-1.71016988	0.69298745	2.49931269
H	0.45667541	-1.84807097	2.58439013
H	-0.99949540	-3.53683175	3.62323942
H	-3.27196834	-3.98731018	2.74554359
H	-5.06859361	-3.47642629	1.05778748
H	-5.85420017	-2.19873470	-0.89576919
H	-5.39082161	-0.41979482	-2.67082026

H	-3.78947668	1.25328036	-3.62296726
H	-1.54889336	1.52427356	-2.56542939
C	2.50647574	-3.30448687	-2.33565835
C	3.02612280	-2.64219231	-1.20542620
C	2.22312422	-1.64461171	-0.60215370
N	0.98314252	-1.31552414	-1.08579183
C	0.51197967	-1.96251827	-2.15821870
C	1.24968292	-2.96169484	-2.80852945
C	4.31381924	-2.90727198	-0.62261638
C	4.74469014	-2.21927252	0.47648269
C	3.93605191	-1.20411515	1.09983240
C	2.66121087	-0.92058125	0.54430897
C	4.33552376	-0.46903567	2.23795111
C	3.48333015	0.49033525	2.76482673
C	2.21683690	0.75507708	2.19408860
C	1.76951818	0.05645516	1.07284610
H	5.72127878	-2.43505970	0.90169913
H	4.93926536	-3.66935035	-1.07795794
H	3.09132802	-4.07694222	-2.82617565
H	0.82021984	-3.45250514	-3.67416419
H	-0.47290441	-1.67460329	-2.50444729
H	5.30448312	-0.65970651	2.69050987
H	3.79404941	1.05512647	3.64035384
H	1.59209406	1.51621220	2.65398665
H	0.66136402	5.25235260	-0.74257847
H	-0.54420620	5.18654814	0.93745912

Table 10S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for 2CA'.

Atom symbol	X	Y	Z
C	5.27918101	0.28711164	0.42432224
C	4.17907582	-0.36984078	1.07909311
C	2.87209388	-0.22317249	0.53886084
C	2.69832385	0.54787492	-0.65373391
C	3.79386260	1.18163261	-1.29225841
C	5.09757042	1.03283455	-0.70483749
N	1.42741003	0.61663091	-1.16686208
C	3.53855863	1.90888561	-2.47182994
C	2.24660318	1.97451942	-2.96648165
C	1.21249238	1.31619594	-2.28725993
C	4.32712802	-1.16243782	2.23890309
C	3.21308323	-1.76709965	2.80104913
C	1.92273439	-1.59562157	2.24734149
C	1.70705221	-0.81408605	1.11132102
H	6.27398568	0.17817924	0.84823525
H	5.93886329	1.52129566	-1.18722931
H	0.19249608	1.34183148	-2.64938165
H	4.35491182	2.40849129	-2.98521525
H	2.01568069	2.52294961	-3.87234719
H	5.31231997	-1.29500557	2.67729973
H	3.33192795	-2.38306232	3.68931306
H	1.08620499	-2.09110815	2.73670000
C	0.64337296	3.60716595	2.02300233
C	-0.41615463	4.37253649	1.56635405
C	0.75709055	2.27327811	1.61236833
C	-1.34330693	3.80554038	0.67024738
C	-2.45736099	4.52155779	0.11219948
C	-1.15361726	2.45383992	0.28238045
C	-3.29229464	3.92899501	-0.79043954
C	-2.01129708	1.82703638	-0.67460214
C	-3.08831756	2.57349709	-1.22675699
C	-1.70121782	0.48954544	-1.05269188
C	-3.89840653	1.94377846	-2.19765553
C	-2.52722999	-0.06973805	-2.02847622
C	-3.61167929	0.64571983	-2.58859680
N	-0.12547042	1.69752012	0.78732139
H	1.38448885	4.01346165	2.70143020
H	-0.53274228	5.40513289	1.88207436
H	-2.61388425	5.55085000	0.42058790
H	1.56290684	1.64680849	1.97156993

H	-4.12597905	4.48762321	-1.20766428
H	-4.73159158	2.48602287	-2.63602334
H	-2.35107600	-1.08192159	-2.38549355
H	-4.22919219	0.16673910	-3.34472294
Ir	-0.04691756	-0.28233910	0.04177989
C	0.45292485	-2.75210429	-1.87029931
C	0.01081435	-3.91737071	-2.50698173
C	-1.16895173	-4.53428418	-2.11930495
N	-0.27343044	-2.18715098	-0.86606787
C	-1.87089547	-3.99294995	-1.05264652
C	-1.40012185	-2.83360611	-0.43397174
N	-1.44824711	-1.19641687	1.33181503
C	-2.04888255	-2.28739124	0.76861542
C	-1.87048910	-0.77541525	2.55444880
C	-3.16215492	-2.89543207	1.34993114
C	-2.97602134	-1.37183147	3.17172754
C	-3.65130797	-2.41490114	2.55686822
H	-2.77245927	-4.47436525	-0.70203220
H	-3.63965501	-3.74201209	0.87715138
H	0.61423331	-4.32772822	-3.30799434
H	-1.52297406	-5.42972985	-2.61822787
H	-4.52066468	-2.86843511	3.02015676
H	-3.28901963	-1.00157791	4.14101074
C	1.75502902	-2.15634553	-2.31581296
H	2.37451839	-1.88756901	-1.46126422
H	1.59910682	-1.26308909	-2.92492733
H	2.29590820	-2.88357886	-2.92345749
C	-1.14819869	0.31638006	3.28709456
H	-0.07197857	0.24058572	3.13630939
H	-1.36164779	0.23420482	4.35474501
H	-1.47838086	1.30525229	2.95995454

Table 11S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for 2BA'.

Atom symbol	X	Y	Z
C	1.66411842	5.00039285	1.03502629
C	1.73466730	3.65929015	1.55409153
C	1.05924286	2.62668700	0.85242268
C	0.33601812	2.94682269	-0.33326767
C	0.27206967	4.26989338	-0.83292894
C	0.96711412	5.29519505	-0.10257846
N	-0.28934034	1.89975528	-0.95985974
C	-0.46812757	4.48865837	-2.01206735
C	-1.09731477	3.41944316	-2.62960856
C	-0.98949912	2.13619890	-2.07528561
C	2.43768964	3.30639942	2.72729408
C	2.44403771	1.98443969	3.14753162
C	1.76211603	0.97270663	2.43285508
C	1.04974887	1.26407080	1.26903711
H	2.18206171	5.79060031	1.57208651
H	0.92592688	6.31369340	-0.47683968
H	-1.47257118	1.28278795	-2.53474232
H	-0.54145618	5.48959641	-2.42709161
H	-1.67609473	3.55326412	-3.53613332
H	2.96651623	4.07023048	3.29039389
H	2.98628209	1.71574178	4.05084731
H	1.79969183	-0.04364305	2.81621720
C	-3.44367015	1.16547150	2.59058652
C	-4.49459114	0.52128400	1.95833241
C	-2.12412570	1.08750280	2.09073598
C	-4.24929562	-0.23003964	0.78751155
C	-5.28746783	-0.92865924	0.07626240
C	-2.91572953	-0.29548527	0.29748938
C	-5.02516290	-1.65091289	-1.05189156
C	-2.65389335	-1.05557099	-0.88925787
C	-3.69022475	-1.73791788	-1.57596202
N	-1.35865578	-1.08447971	-1.32518156
C	-3.34217880	-2.45996439	-2.73614092
C	-1.05769456	-1.77646307	-2.42614905
C	-2.02435748	-2.47921856	-3.16131932
C	-1.81982332	0.35789179	0.94069634
H	-3.63425679	1.74444110	3.49090070
H	-5.50509246	0.58708598	2.35189359
H	-6.30255861	-0.87142135	0.46024885
H	-1.33500646	1.60905848	2.62426329

H	-5.82222066	-2.17188496	-1.57421097
H	-4.10998532	-2.99456866	-3.28795612
H	-0.01772467	-1.76795948	-2.73443481
H	-1.72547298	-3.02429151	-4.04934717
Ir	-0.01627989	0.06312428	0.01091133
C	2.44289752	0.12251765	-1.98448667
C	3.62378158	-0.32805892	-2.55645868
C	4.21097482	-1.51376449	-2.09290909
N	1.82187705	-0.53624000	-0.99071222
C	3.55704729	-2.18846608	-1.05869253
C	2.36883651	-1.68545869	-0.52149132
N	0.48704817	-1.70748295	0.98651289
C	1.62085917	-2.34141629	0.57259837
C	-0.23654676	-2.25875859	1.98280560
C	2.02688838	-3.53844859	1.16671739
C	0.12602504	-3.44365866	2.60300846
C	1.28586919	-4.11798107	2.19868430
H	3.98312089	-3.10795292	-0.67643203
H	2.92944202	-4.02948126	0.82496175
H	4.08024704	0.24436464	-3.35699152
H	-0.49883162	-3.83460881	3.39891893
H	1.96632630	1.03556559	-2.32203437
H	-1.12465064	-1.71457067	2.27624451
C	5.49366546	-2.03182597	-2.68493042
H	5.38929615	-2.17774529	-3.76499860
H	5.78944369	-2.98133445	-2.23447558
H	6.30452016	-1.31114394	-2.53420810
C	1.71111590	-5.40505828	2.85072475
H	2.61360010	-5.81038588	2.38903520
H	0.91673358	-6.15506633	2.77805631
H	1.90927963	-5.24823917	3.91642521

Table 12S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for 2DA'.

Atom symbol	X	Y	Z
C	-2.73905343	-4.59399362	-1.36086477
C	-1.72053156	-3.69581133	-1.83008341
C	-1.44210522	-2.53616350	-1.06254711
C	-2.14870942	-2.25588328	0.15306591
C	-3.15036392	-3.16724909	0.58801040
C	-3.42010137	-4.33678702	-0.20629380
C	-1.80780534	-1.07301793	0.87866177
C	-3.83775436	-2.88183148	1.78852184
C	-3.52155718	-1.73729797	2.50213396
C	-2.52237010	-0.84351492	2.05547083
C	-0.97687662	-3.89343468	-3.01181342
C	-0.01659013	-2.96587005	-3.37962911
C	0.19721308	-1.84277071	-2.56595943
N	-0.49215290	-1.62964361	-1.44308088
H	-2.95607082	-5.48269588	-1.94611404
H	-4.18798971	-5.02574055	0.13565257
H	-2.31259504	0.03942277	2.65183156
H	-4.60735653	-3.56266228	2.14138438
H	-4.05169630	-1.51855503	3.42585045
H	-1.16291061	-4.77081648	-3.62460766
H	0.57116547	-3.08911119	-4.28209190
H	0.93856719	-1.09549293	-2.82796999
C	-3.44962574	1.85917715	-2.49209157
C	-3.74512099	3.01668742	-1.78969540
C	-2.47229396	0.98088572	-2.00317281
C	-3.05652921	3.29507223	-0.59205155
C	-3.27202332	4.46015802	0.22281847
C	-2.08300263	2.36166389	-0.16185496
C	-2.55960019	4.65803841	1.37187937
C	-1.33397260	2.55624454	1.03505502
C	-1.56724915	3.71574566	1.81970526
C	-0.38370279	1.54993469	1.37442890
C	-0.80766668	3.87481838	2.99991212
C	0.34044084	1.76081893	2.54854995
C	0.12583292	2.90867525	3.34597534
N	-1.80151504	1.22212657	-0.87073493
H	-3.96119892	1.61483991	-3.41584865
H	-4.49993706	3.70762805	-2.15337638
H	-4.01636288	5.18335790	-0.09697948
H	-2.22116051	0.06858888	-2.52968778

H	-2.73817548	5.54570174	1.97299857
H	-0.95932388	4.74967622	3.62581771
H	1.08280323	1.03710766	2.87551547
H	0.70944788	3.03413762	4.25477673
Ir	-0.31967036	0.03529058	0.00938913
C	1.16844214	-1.92485246	1.82724065
C	2.25108140	-2.57450911	2.38299803
C	3.54558805	-2.21322582	1.97508126
N	1.28981212	-0.94508173	0.90241327
C	3.67951762	-1.19682693	1.02116683
C	2.54024333	-0.57907262	0.50496920
N	1.40791588	0.96474447	-0.93535951
C	2.60729880	0.50671457	-0.50243807
C	1.38393370	1.95422542	-1.85063569
C	3.81054715	1.03242478	-0.97758134
C	2.52814451	2.52418972	-2.37281817
C	3.77837782	2.05987807	-1.92981684
H	4.65752693	-0.89266180	0.67992942
H	4.75359579	0.65557182	-0.61029413
H	2.10827297	-3.35459963	3.12093892
H	2.47091509	3.31868729	-3.10706116
H	0.15704001	-2.17651009	2.11785784
H	0.40295834	2.29087603	-2.16489103
O	4.56399273	-2.87880344	2.53758018
O	4.85941080	2.64949053	-2.46177812
C	5.90811793	-2.55229259	2.15357875
H	6.54691610	-3.21353215	2.73710893
H	6.14068281	-1.51013027	2.39310740
H	6.06513488	-2.73663849	1.08634009
C	6.16464544	2.22459277	-2.04356880
H	6.32941055	1.17020094	-2.28591251
H	6.30474099	2.39010746	-0.97093728
H	6.86565554	2.84210841	-2.60322883

Table 13S. Cartesian coordinates from the optimized structures of S_0 in CH_3CN media for 2EA'.

Atom symbol	X	Y	Z
C	-3.83251042	2.66542632	-2.94478520
C	-2.78693262	1.68163963	-3.02719842
C	-1.99626259	1.46127990	-1.87365638
C	-2.21412387	2.18687782	-0.66588598
C	-3.25486799	3.15033226	-0.61233154
C	-4.05338635	3.36356358	-1.79124373
C	-1.35692396	1.88966634	0.43304461
C	-3.44549662	3.84617911	0.60209791
C	-2.62263622	3.56998952	1.68395798
C	-1.58899686	2.60786175	1.60643884
C	-2.49209056	0.92126780	-4.17674290
C	-1.45773925	-0.00000162	-4.13713276
C	-0.72079938	-0.16519538	-2.95583611
N	-0.97870498	0.54307472	-1.85085859
H	-4.44585250	2.84175090	-3.82343378
H	-4.84975314	4.10192259	-1.74959821
H	-0.97295598	2.43878440	2.48556433
H	-4.23304931	4.59041058	0.67938933
H	-2.77136358	4.10795173	2.61698782
H	-3.07411487	1.06206954	-5.08270885
H	-1.20397013	-0.59993613	-5.00338858
H	0.09440041	-0.87611353	-2.89793795
C	2.62265508	3.56997079	-1.68397095
C	3.44551638	3.84616183	-0.60211192
C	1.58901214	2.60784720	-1.60644795
C	3.25488501	3.15032070	0.61232038
C	4.05340414	3.36355372	1.79123174
C	2.21413714	2.18687054	0.66587878
C	3.83252548	2.66542200	2.94477607
C	1.99627270	1.46127878	1.87365229
C	2.78694368	1.68163990	3.02719339
N	0.97871113	0.54307784	1.85085835
C	2.49209861	0.92127384	4.17674093
C	0.72080297	-0.16518712	2.95583857
C	1.45774373	0.00000827	4.13713445
C	1.35693624	1.88965768	-0.43305069
H	2.77138464	4.10792848	-2.61700306
H	4.23307197	4.59038991	-0.67940639
H	4.84977381	4.10190945	1.74958325
H	0.97297083	2.43876831	-2.48557283

H	4.44586829	2.84174776	3.82342391
H	3.07412362	1.06207676	5.08270624
H	-0.09439959	-0.87610233	2.89794318
H	1.20397241	-0.59992196	5.00339260
Ir	0.00000261	0.42984503	0.00000032
C	-2.47669229	-1.22317591	1.00626712
C	-3.27861889	-2.35248569	1.28996988
C	-2.72082863	-3.64177647	1.03262552
N	-1.24639001	-1.30323149	0.52096437
C	-1.40617171	-3.69886556	0.51440568
C	-0.68978479	-2.54402686	0.26839498
N	1.24638393	-1.30324171	-0.52095612
C	0.68976822	-2.54403252	-0.26838710
C	2.47668734	-1.22319646	-1.00625769
C	1.40614551	-3.69887718	-0.51439783
C	3.27860449	-2.35251297	-1.28996057
C	2.72080302	-3.64179913	-1.03261737
C	-4.59399039	-2.23942096	1.80972067
C	-5.32746931	-3.37714723	2.06322875
C	-4.77639747	-4.65998226	1.80816167
C	-3.50140313	-4.79619954	1.30372228
C	3.50136757	-4.79622876	-1.30371489
C	4.59397706	-2.23945919	-1.80971095
C	5.32744613	-3.37719162	-2.06321983
C	4.77636319	-4.66002210	-1.80815393
H	-5.00792835	-1.25391097	2.00097298
H	-6.33434724	-3.29859923	2.46029898
H	-5.37200862	-5.54365086	2.01506086
H	-3.08208109	-5.77860058	1.10935555
H	5.37196676	-5.54369563	-2.01505379
H	3.08203703	-5.77862635	-1.10934912
H	5.00792363	-1.25395265	-2.00096239
H	6.33432486	-3.29865199	-2.46028981
H	-2.85759277	-0.22309268	1.18815267
H	-0.97257135	-4.67069145	0.31212877
H	0.97253683	-4.67069941	-0.31212122
H	2.85759673	-0.22311645	-1.18814235

Equation 1S.

$$E_g^{exp.} = 0.228*E1 + 2.144*E2 + 0,349*E3 - 16,532$$

E1- energies for the real system with the low method

E2 - energies for the high layer with the high method

E3 - energies for the high layer with the low method

Table 14S.

Absolute energies computed within ONIOM scheme for the studied compounds with charge +1 (E_1-E_3) and with charge +2 (E_4-E_6) together with calculated oxidation potential $E_{ox\ calc.}$ and experimental oxidation onset potential $E_{ox\ onset}$

Compound	E_1 [a] [hartree]	E_2 [b] [hartree]	E_3 [c] [hartree]	E_4 [d] [hartree]	E_5 [e] [hartree]	E_6 [f] [hartree]	$E_{ox\ calc.}$ [g] [V]	$E_{ox\ onset}$ [V]
2AA'	-1679,371355	-635,0301737	-624,4302032	-1679,231263	-634,9573767	-624,4800436	0.69	0.69
2BA'	-1756,580234	-635,208135	-624,6914546	-1756,402985	-634,9582285	-624,4798084	0.51	0.47
2CA'	-1756,536345	-635,1744322	-624,662409	-1756,421302	-634,923416	-624,4813829	0.46	0.47
2DA'	-1904,252478	-635,2086723	-624,6926713	-1904,155965	-634,9588083	-624,483638	0.45	0.49
2EA'	-1981,002555	-635,1930058	-624,6733771	-1980,852125	-634,9227543	-624,4621099	0.49	0.47
2FA'	-1754,232229	-635,1960287	-624,6805641	-1754,042816	-634,9388459	-624,5364009	0.71	0.73
2GA'	-2207,703412	-635,1760963	-624,6561876	-2207,513396	-634,9196263	-624,5077704	0.46	0.51
2HA'	-2284,898198	-635,1827756	-624,6702564	-2284,76386	-634,9209821	-624,53894	0.46	0.41

[a] E_1- energy for the real system at the low accuracy method for a complex with charge +1

[b] E_2 - energies for the real system at the high accuracy method for a complex with charge +1

[c] E_3 - energies for the small model system at the low accuracy method for a complex with charge +1

[d] E_4- energies for the real system at the low accuracy method for a complex with charge +2

[e] E_5- energies for the real system at the high accuracy method for a complex with charge +2

[f] E_6- energies for the small model system at the low accuracy method for a complex with charge +2

[g] $E_{ox\ calc.} = c_0 + \sum_{i=1}^{6} c_i E_i$ where c_0=-2194.95, c_1=-0.059, c_2=5.085, c_3=-3.208, c_4=0.059, c_5=-17.875, c_6=12.698

Figure 1S. Calculated oxidation potential (vertical) *vs* experimental oxidation onset potential (horizontal) for studied compounds.

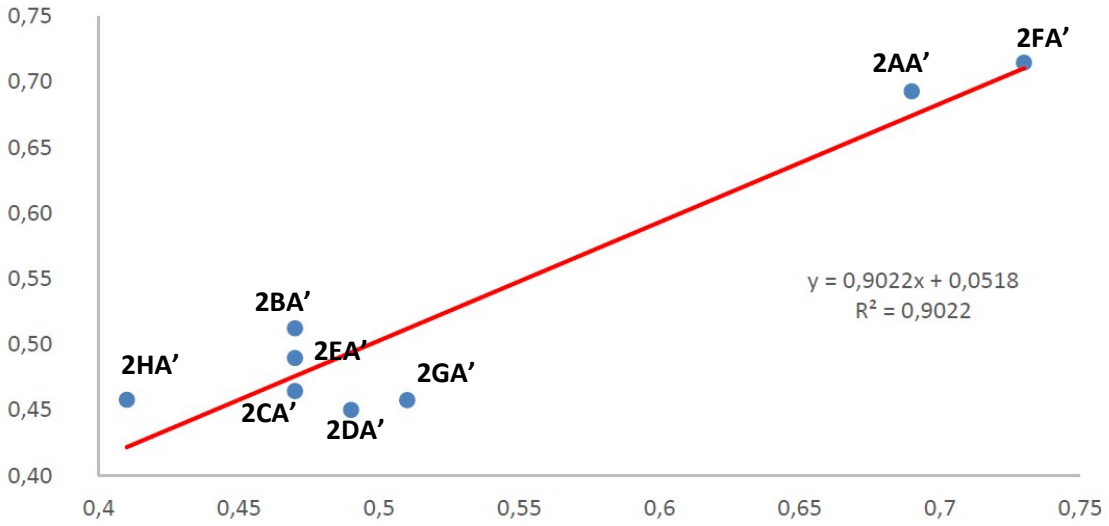
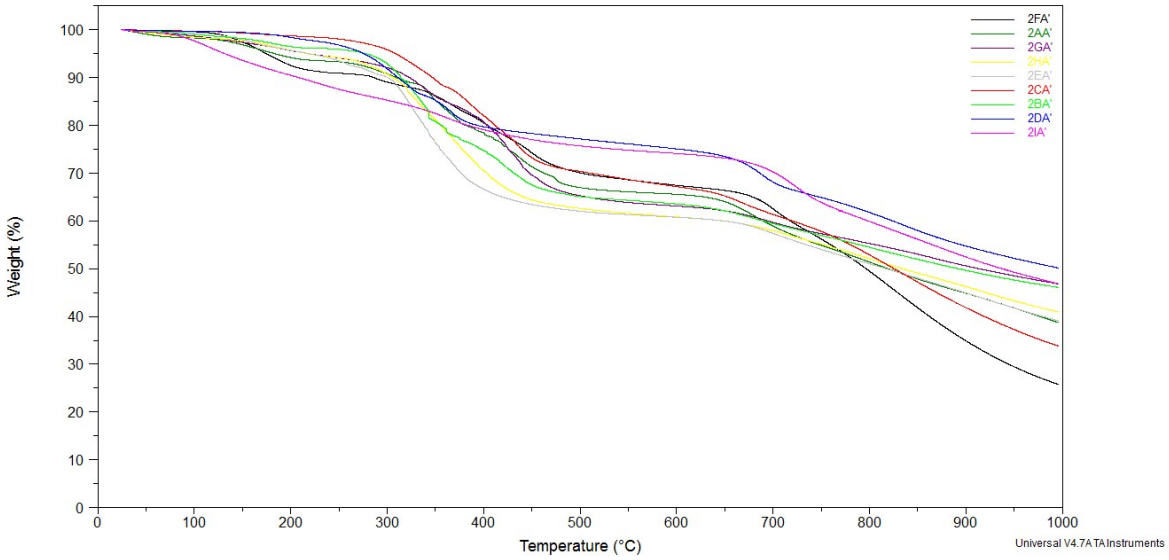


Table 15S. Crystal data, data collection and structure refinement

Compound	**2AA'**	**2FA'**
Formula	$C_{36}H_{24}IrN_4 \cdot PF_6 \cdot C_2H_4Cl_2$	$C_{38}H_{24}IrN_4 \cdot PF_6 \cdot CH_3OH$
Formula weight	948.71	905.82
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
a(Å)	12.7207(5)	12.1984(5)
b(Å)	14.4809(6)	14.8577(5)
c(Å)	18.6448(12)	18.2375(7)
β(º)	93.662(5)	101.868(4)
V(Å^3)	3427.5(3)	3234.7(2)
Z	4	4
D_x(g cm^{-3})	1.84	1.86
F(000)	1856	1776
μ(mm^{-1})	4.17	4.25
Θ range (^{0})	3.13 – 26.79	3.41 – 28.27
Reflections:		
collected	7381	11744
unique (R_{int})	8471 (0.021)	3565 (0.015)
with I>2σ(I)	7235	3141
R(F) [I>2σ(I)]	0.039	0.021
wR(F^2) [I>2σ(I)]	0.089	0.069
R(F) [all data]	0.047	0.025
wR(F^2) [all data]	0.091	0.0732
Goodness of fit	1.10	1.04
max/min Δρ (e Å^{-3})	1.96/-1.63	1.37/-0.96

Figure 2S. TGA curves

a)



b)